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Mean Field and Monte Carlo Modeling of Multiblock Copolymers

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It is well known that, for most conditions of practical interest, mixtures of two different homopolymers A_m and B_n are thermodynamically incompatible; i.e., they spontaneously separate like oil and water due to a positive free energy of mixing. Here A_m denotes a linear sequence of m monomers of type A, and similarly for B_n . A and B may differ in chemical structure (e.g., $-\text{CH}_2-$ and $-\text{CHCH}_3\text{CH}_2-$) or, indeed, simply by isotopic composition (e.g., $-\text{CH}_2-$ and $-\text{CD}_2-$). A *diblock copolymer*, in which a polymer chain A_m is chemically bound at one end to another segment B_n to yield a single chain of length $N = m + n$, is denoted by $A_m B_n$. In this case, complete phase separation is impossible since the two constituents are physically connected. This leads to a complicated morphology that depends sensitively on composition, i.e., the ratio m/n , strength of the interactions between A and B, and temperature. Consequently, the phase diagram for diblock copolymers is extremely rich, and has been the subject of extensive theoretical and experimental study. (See Figure 1.)

While most preceding research into the physics of copolymers has been restricted to diblock systems, these are simply the limiting case of the more general case $(A_m B_n)_p$ corre-

Nonetheless, multiblock copolymers have received only limited attention in the literature. They are of keen interest to us, however, since they represent to a rather high degree of approximation the physical situation encountered in some polymer-based materials relevant to DOE; for example, Estane™-based binders found in certain plastic-bonded explosive formulations such as PBX-9501. Our goal is to un-

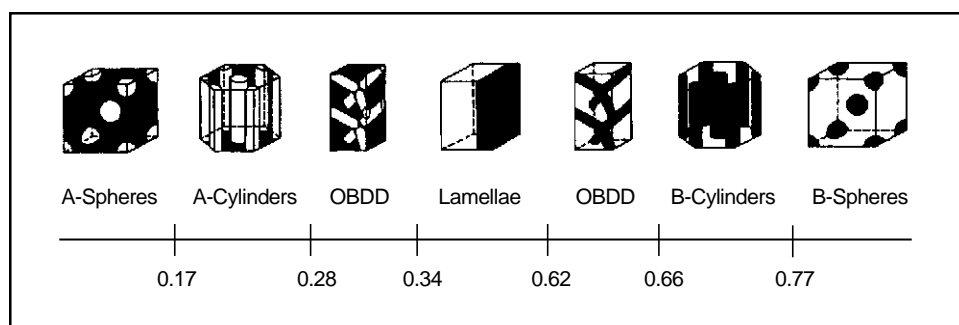


Figure 1: Schematic illustration of morphological complexity in idealized microphase separated diblock copolymers as a function of composition variable (“abscissa”) $\phi = m/(m + n)$.*

derstand the morphology and associated elastomeric properties of as-manufactured Estane™ in the “bulk,” and the adhesive properties at the explosive crystal/binder interface. Moreover, we need to develop the ability to predict the effects of *aging*, which in the case of Estane™ corresponds primarily to a decrease in chain molecular weight, on those elastomeric and adhesive properties.

In order to be truly predictive, our understanding of Estane™ and other systems must be expressed in terms of fundamental chemical interactions and statistical mechanical analyses at the chain level. Direct simulations at such scales are impractical, however, due to the large spatial and temporal relaxations associated with polymeric materials. Thus, we must develop a *multiscale modeling capability* in which information generated at relatively fundamental scales is incorporated into successively more coarse-grained ones, via a sequence of “upscaling” or homogenization approaches. Of course, each upscaling step has associated with it a decrease in the level of chemical and/or physical detail retained.

Comparison of results obtained from the two approaches is meaningful because the parameter specification is the same in each case, and agreement between the two provides a mutual validation of the tools.

sponding to p diblocks bound end-to-end; we refer to these as *multiblock copolymers*. Although the phase diagram of a multiblock copolymer melt is expected to be reminiscent of the diblock case, they will certainly differ in detail.

Thus, a crucial issue is that of identifying the essential features that must be included at a given stage without compromising the salient physics in the overall process.

As one step towards this goal, we have adapted a mean-field theory originally developed for diblock copolymers by Leibler [1] to the case of multiblock systems. Within the framework of this modified Leibler theory, one must specify the primary structure of the multiblock polymer of interest, i.e., m , n , and p . It is also necessary to specify the short-range interaction energy χ acting between distinct monomer types A and B , and overall system density ρ . As a test of the theory, and to enable study of chain-level statistical properties not accessible in the mean-field treatment, we have performed complementary calculations using a lattice Monte

Carlo model for polymers known as the bond fluctuation method (BFM) [2]. Comparison of results obtained from the two approaches is meaningful because the parameter specification is the same in each case, and agreement between the two provides a mutual validation of the tools (Figure 2).

Among the quantities of interest to us at this stage of our research are the p -dependencies of: (1) the structure factor—a measure of the spatial scale for concentration fluctuations in the material (Figure 2); (2) the microphase separation transition temperature at which the melt passes from a spatially heterogeneous to a spatially homogeneous state; and (3) the detailed statistical properties of the chains in a given morphological state (Figure 3). Each of the preceding is treated as a parametric function of the ratio m/n .

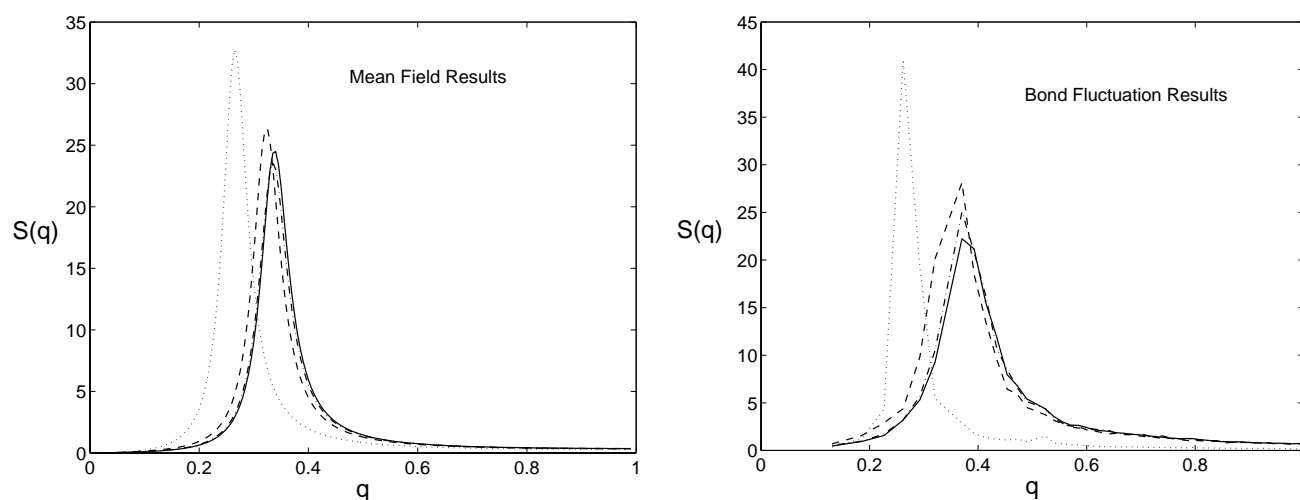


Figure 2: Comparison of structure factors for symmetric ($m = n$) multiblock copolymers based on modified Leibler theory (left panel) and bond fluctuation Monte Carlo (right panel), as a parametric function of the block factor p .

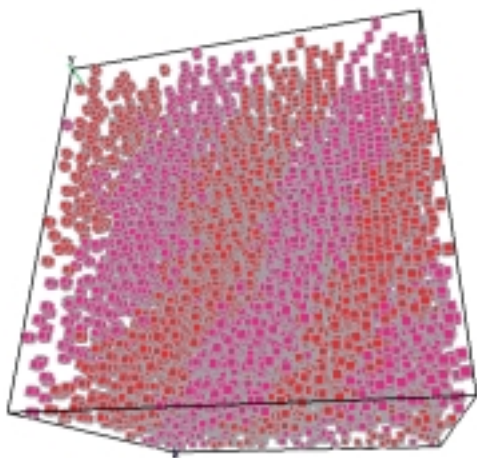


Figure 3: Snapshot from a bond fluctuation Monte Carlo realization for a symmetric multiblock system ($p = 6$), illustrating the lamellar phase expected for that material composition.

Future research will focus on more complex architectures, e.g., linear, brush, star, or triblock materials; and the effects of polydispersity (i.e., variations in chain length), plasticization, and interfaces on the properties of the material.

**Figure from "The physics of polymers: concepts for understanding their structures and behavior" by G. Strobl (Springer, Berlin, 1996).*

[1] L. Leibler, *Macromolecules* **13**, 1602 (1980).

[2] K. Ø. Rasmussen, T. D. Sewell, T. Lookman, and A. Saxena, "Mean Field and Monte Carlo Modeling of Multiblock Copolymers." to appear in Proceedings of the 2000 Fall National Meeting of the Materials Research Society. (LA-UR-01-0091.)

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